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Application of the equilibrium theory to ternary moving bed configurations (4+4, 5+4, 8 and 9 zones) II. Langmuir case

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Abstract

In this article, the overall methodology used to determine the working flow-rates of a true moving bed (TMB) processing langmuirian isotherms compounds is explained. Then it is applied to different ternary configurations (4+4, 5+4, 8 or 9 zones TMB) in order to characterize their performances. Finally the results obtained on all the configurations are compared on a given example. This comparison allows the choice of the more suitable configuration to be used for a given set of compounds.

Keywords: Equilibrium theory; Adsorption isotherms; Ternary moving bed; True moving bed; Simulated moving bed chromatography

1. Introduction

The simulated moving bed (SMB) process introduced by Broughton in 1961 [1] for petrochemical separations is the real application of the corresponding theoretical concept the true moving bed (TMB). This concept is based upon the addition of a counter-current motion of the stationary phase in comparison to the mobile phase in order to enhance the separation performances. The use of this process for pharmaceutical oriented separations has been made possible thanks to the application of the equilibrium theory to the theoretical TMB fractionating a mixture of compounds characterized by Langmuir adsorption isotherm. Anyway, the classical TMB process knows two inlet streams called feed and eluent and two outlet streams called raffinate and extract, ordered in the following way: eluent, extract, feed and raffinate, thus delimiting four different zones between each couple of inlet/outlet stream. This classical configuration is clearly able to separate a binary mixture into two pure fractions. As far as ternary mixtures are concerned, if the compound of interest is either the less or the most retained one, it is possible to do so with the classical four zones TMB process. However, in case the middle compound is of main interest, it is not possible to perform its production in one pass. Consequently a second TMB may be added to perform the remaining separation. Therefore, the objective of this work is to make the comparison of the performances of differ-

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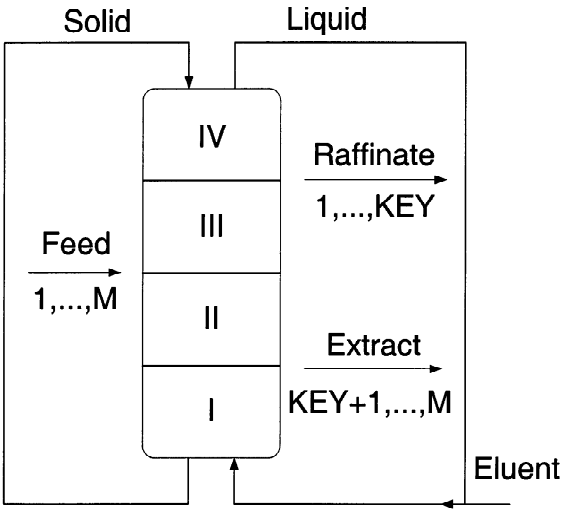

Fig. 1. Classical 4-zone TMB processing a multi-component mixture.

ent ternary TMB configurations working in two pass. The complete results of this study have been presented in Part I of this article for the linear case [2], which means that the TMB processes had to fractionate a mixture of compounds characterized by a linear adsorption isotherm. In Part II, the mixture of compounds is characterized by a classical multi-component Langmuir adsorption isotherm. As just stated, all the different ternary TMB configurations studied in this article involve two TMB working in a row, each TMB having either four (Fig. 1) or five zones (Fig. 2) [3]. The first TMB fractionates the ternary mixture into two different streams, and the second TMB fractionates the two remaining non-separated compounds. As a matter of fact, the two TMB involved in the process can be either separated (Figs. 3 and 4) or part of a single device (Figs. 5 and 6) [4,5]. On Fig. 1, one can introduce the KEY compound concept, which can, respectively, be equal to 1 or 2 if compound 1 or 3 is separated from (2,3) or (1,2). Consequently, when this concept is applied to the two TMB in a row configurations, there are two ways of fractionating the ternary mixture (1,2,3) as illustrated in Figs. 2–6. The study of a TMB means the determination of the working flow-rates in every zone in order to get purified product in the required stream (extract or raffinate). In order to determine the working flow-rates, it is possible to apply the methodology presented in Part I for the linear case. In other words, the migration directions of every compound in each zone is first set in order to get pure compounds in the desired streams. Then the equilibrium theory is applied to express these conditions in terms of flow-rates ratio m intervals in every zone. These variables will be expressed in function of known parameters such as the feed concentrations and the adsorption parameters of every compound. After having determined all the possible working flow-rates of a given configuration, it is compulsory to choose one common point for all the configurations in order to compare their performances. For some configurations, it is not possible to get analytical expressions of their performances, therefore the general comparison of all the configuration performances can be obtained only numerically as will be explained further.

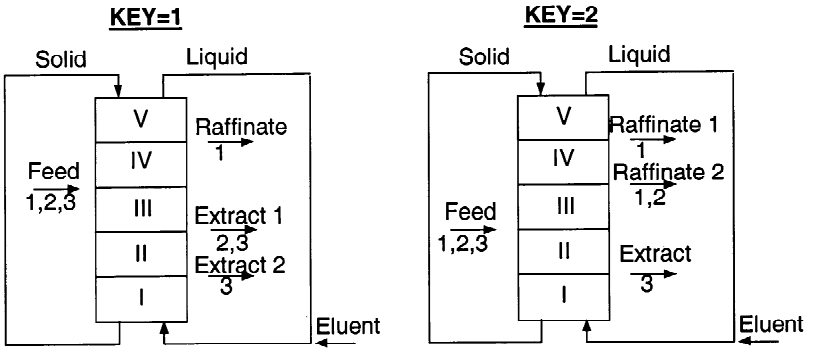

Fig. 2. Five-zone TMB processing a ternary mixture.

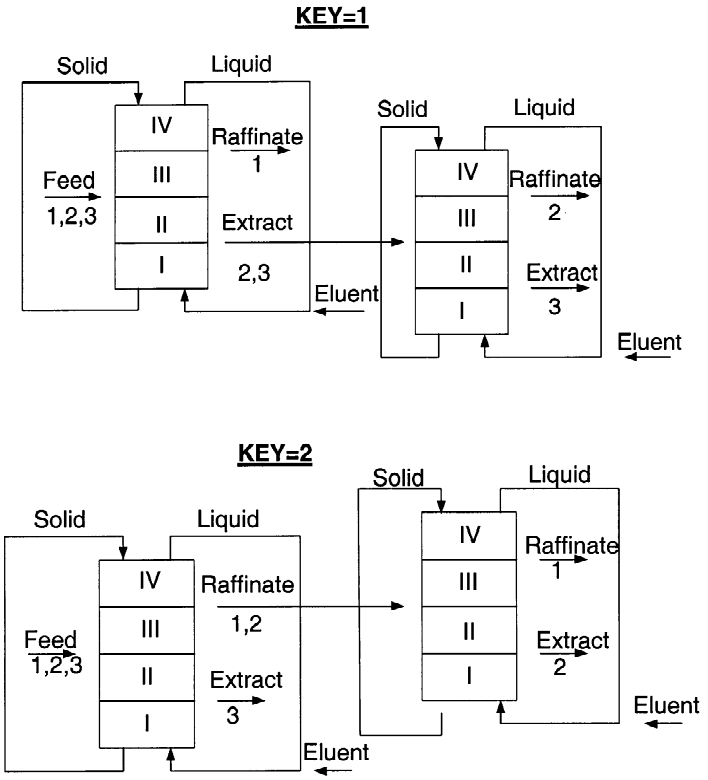

Fig. 3. 4+4-zone TMB configurations.

As the general methodology to be applied has already been explained in Part I of the article [2] before, in the upcoming parts, we will focus more on the application of the equilibrium theory to all the different chromatographic processes involved in this study, going from a classical four-zone to a nine-zone TMB process. A performances comparison will then be presented on a given numerical example.

2. Application of the equilibrium theory

2.1. General assumptions and results

In this study, we assume to work with a ternary mixture of components 1–3 with ascending affinity for the solid-phase. The mobile phase is liquid and non-adsorbed. The retention behavior of the compounds with the solid stationary phase is characterized by a classical multi-component Langmuir isotherm:

$$n_i = \frac{N_i K_i C_i}{1 + \sum_j K_j C_j}, \quad i = 1,2,3 \tag{1}$$

We can introduce here the parameter D standing for the denominator of the Langmuir isotherm:

$$D = 1 + \sum_j K_j C_j \tag{2}$$

The equilibrium theory is based upon the ideal column concept [6]. In our case, we will consider the following assumptions to be observed:

- isothermal and isochore
- one directional flow
- constant volumetric flow
- constant porosity
- no channeling
- no axial dispersion
- no kinetics resistance
- local equilibrium established everywhere.

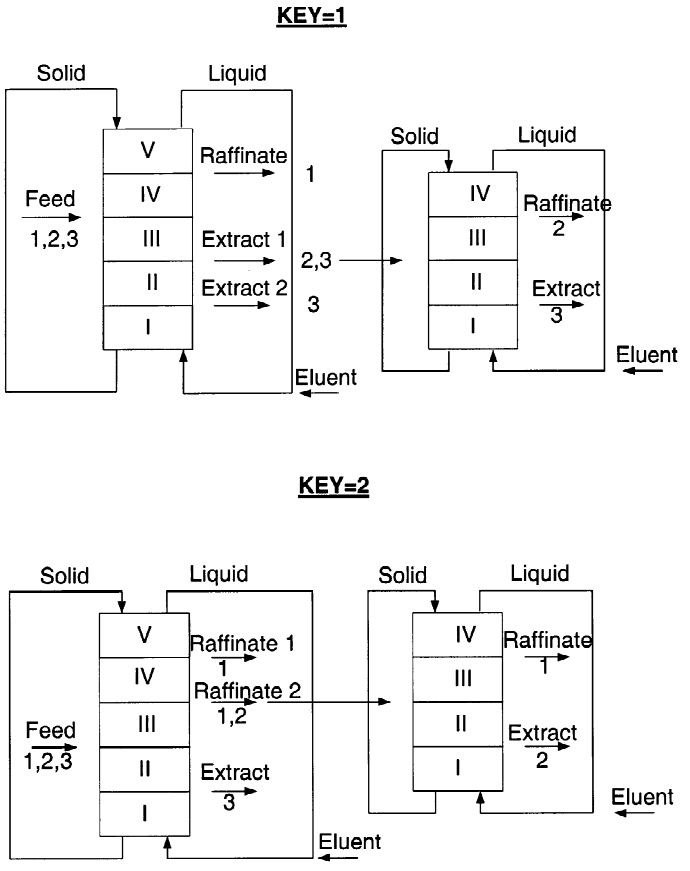

Fig. 4. 5+4-zone TMB configurations.

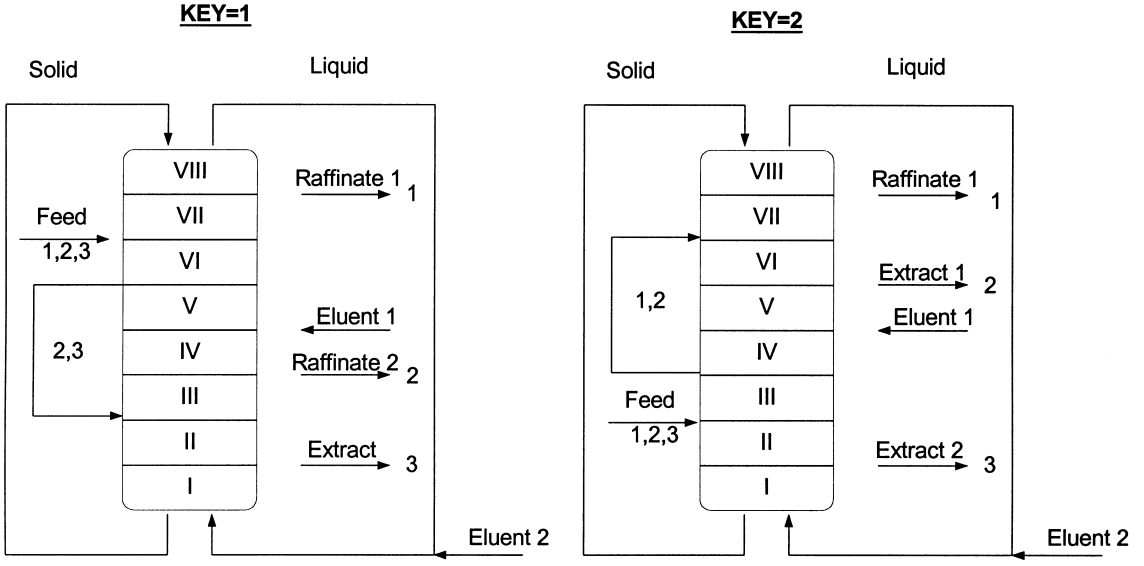

Fig. 5. Eight-zone TMB configurations.

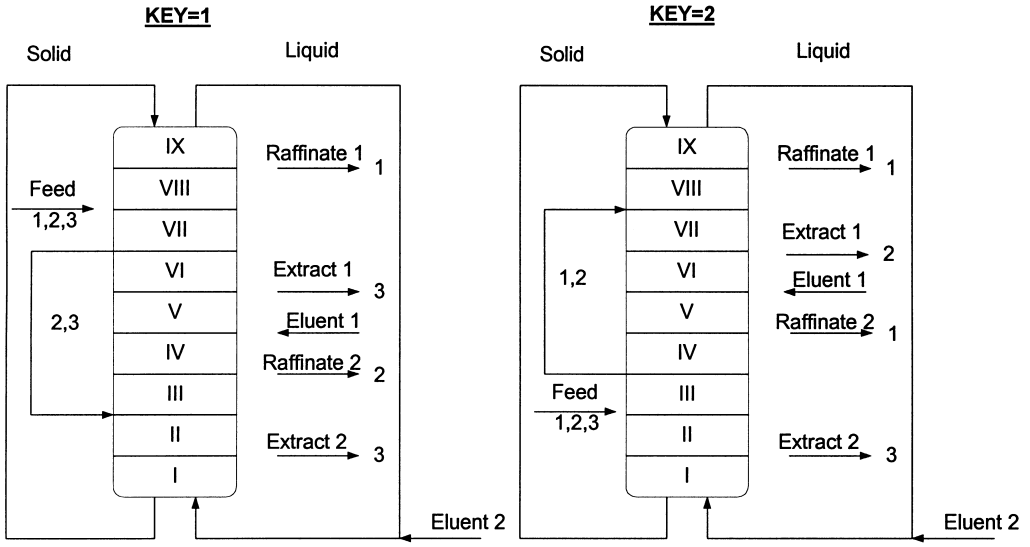

Fig. 6. Nine-zone TMB configurations.

The application of the equilibrium theory to a counter current column has been performed by Rhee et al. [7] and can be used to determine the evolution of the concentration profile inside the column over the time and at steady state for any given initial conditions.

The system of equations resulting from mass balances of each compound on the column cannot be solved analytically in the concentration space because of the coupling induced by the Langmuir isotherm. However, it is possible to decouple these equations thanks to a base change. In the corresponding space, an explicit solution to the system can be found. The solutions can be given as functions of the ω values, which are compositions, hence combinations of concentrations. The relationship between the concentration space and the ω space is called the characteristic equation and can be expressed as follows:

$$\sum_{i=1}^{3} \frac{K_i n_i}{N_i K_i - \omega} = 1. \tag{3}$$

This relationship can be written in terms of concentrations in the liquid phase by substituting Eq. (1):

$$\omega \sum_{i=1}^{3} \frac{K_i C_i}{N_i K_i - \omega} = 1. \tag{4}$$

The ω values solution to this equation verify Eq. (5):

$$0 \leq \omega_1 \leq N_1 K_1 \leq \ldots \leq \omega_3 \leq N_3 K_3 \tag{5}$$

As a matter of fact there exists a reverse bijective function to the characteristic Eq. (3) which can be used to calculate the liquid concentrations in function of the ω variables:

$$c_i = \frac{1}{K_j} \cdot \frac{\prod_{j=1}^{3} \left(\frac{N_i K_i}{\omega_j} - 1 \right)}{\sum_{\substack{j=1 \\ j \neq 1}}^{3} \left(\frac{N_i K_i}{N_j K_j} - 1 \right)}, \quad \forall i \in [1,3] \tag{6}$$

This relationship can also be written for the concentrations in the solid-phase by substituting Eq. (6) in (1):

$$n_i = \frac{1}{K_i} \cdot \frac{\prod_{j=1}^{3} (N_i K_i - \omega_j)}{\sum_{\substack{j=1 \\ j \neq 1}}^{3} (N_i K_i - N_j K_j)}, \quad \forall i \in [1,3] \tag{7}$$

Eqs. (3)–(7) link the concentrations (liquid or solid) of one stream and their corresponding ω variables. The equilibrium theory has been successfully applied to a classical four-zone TMB processing binary mixtures by Storti et al. [8], multi-component mixtures by Mazzotti et al. [9] and with other working

conditions [10–14]. As a matter of fact, for all the TMB configurations considered in our study, we will encounter only two specific cases of the application of the equilibrium theory to a counter current column. The first case corresponds to the saturation of a clean bed by a liquid stream containing M compounds, which will generate M shock waves inside the column, separating $M+1$ different concentration states. The second case corresponds to the elution of a bed saturated with M compounds with a clean liquid stream, which will generate M dispersive waves inside the column separating $M+1$ different concentration states. Moreover, as already stated in Part I of this article, in order to produce pure compounds with a TMB process, it is compulsory to make the different compounds migrate in a given direction, meaning that they will have to follow either the liquid or the solid stream in a given zone. In order to do so, inside every zone, a specific concentration state is required. This means that one of the two surrounding waves (shock or a composition of the dispersive wave) may be stabilized inside the zone. It can be performed by choosing carefully the value of the flow-rate ratio m between two different border values corresponding to each wave. This will lead to different working intervals for the flow-rates ratios m in every zone knowing that these border values are expressed as functions of the ω variables of the system and need to be expressed in terms of known parameters being the retention parameters and the feed concentrations. To solve this problem, it is required to write mass balance equations on the feed node and on the different zone interfaces being either their inlet or their outlet side. This leads to a system of non-linear equations, which can be solved numerically. In order to have an analytical resolution, it is compulsory to simplify the system of equations (using binary mixtures for example [8]), or using ternary mixtures as will be demonstrated in this article. The resolution of this system of equations for a specific point inside the working intervals leads to the complete characterization of the system at this specific point. Consequently, to determine the entire working region of a TMB process, this resolution has to be performed for all the possible working points. Finally, in order to compare all the TMB performances, it is compulsory to perform their determination at the same working point and in our study, we have decided to work with the low solvent consumption (LSC) point that we define as the one able to give the highest value of R defined as the ratio of the feed flow-rate over the eluent flow-rate. The application to the different ternary TMB configurations will now be reviewed.

2.2. Two four-zone TMB in a row

In this part, we will focus on the determination of the working flow-rates of the two TMB involved in this configuration at the LSC point. We introduce the different streams involved in a classical four-zone TMB processing a multi-component mixture (Fig. 7). It is interesting to remind the expression of the working intervals of the flow-rate ratios m for a multicomponent mixture in function of the ω variables of the system, which will have to be determined (Table 1) [9]. It is also useful to consider the characteristic Eq. (1) and perform its resolution

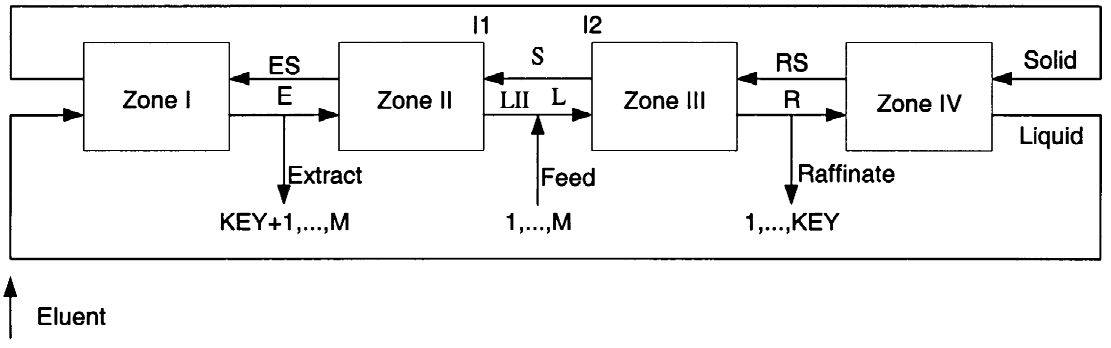

Fig. 7. Liquid and solid streams involved in a TMB process.

Table 1
Working flow-rate ratios intervals of a classical four-zone TMB

Zone	Flow-rate ratio interval
I	$m_{\mathrm{I}} \geq N_M K_M$
II	$N_{\mathrm{KEY}} K_{\mathrm{KEY}} \cdot \prod_{j=\mathrm{KEY}+1}^{M} \frac{\omega_{\mathrm{S},j}}{N_j K_j} \leq m_{\mathrm{II}} \leq \omega_{\mathrm{S,KEY}+1} \cdot \prod_{j=\mathrm{KEY}+1}^{M} \frac{\omega_{\mathrm{S},j}}{N_j K_j}$
III	$N_{\mathrm{KEY}} K_{\mathrm{KEY}} \cdot \prod_{j=1}^{\mathrm{KEY}} \frac{\omega_{L,j}}{N_j K_j} \leq m_{\mathrm{III}} \leq \omega_{L,\mathrm{KEY}+1} \cdot \prod_{j=1}^{\mathrm{KEY}} \frac{\omega_{L,j}}{N_j K_j}$
IV	$m_{\mathrm{IV}} \leq \omega_{L,1}$

on the feed stream for given feed concentrations and retention parameters in order to determine the corresponding ω variables. This simply means that from this point, we will consider this resolution performed, and the obtained ω_F variables of the feed stream become known parameters. Storti et al. [8] have demonstrated two rules concerning the ω parameters, which simplify the system of equations all throughout the discussion.

(i) Rule 1: on a specific zone, if there exists an ω value common to the inlet stream (feed side) and to the inside concentration state of the zone, this value is also common to the outlet stream (feed side) of the zone.

(ii) Rule 2: around the feed node, there exist two different liquid streams, and if an ω value for a given compound is common to these two liquid streams, then this value is also common to the feed corresponding ω parameter.

From this point, we will refer to these two results as the omega rules.

2.3. First four-zone TMB (ternary)

CASE KEY=1

In order to make the desired TMB process work at the LSC point, the correct waves have to be stabilized in every zone. It means that we have to use the results shown in Table 1 for $M=3$ and KEY=1 and choose the highest border values of m_{III} and m_{IV} as well as the lowest border values for m_{I} and m_{II}. This application results in the following values of the four different flow-rate ratios m in every zone:

$$m_{\mathrm{I}} = N_3 K_3 \tag{8}$$

$$m_{\mathrm{II}} = \frac{N_1 K_1 \omega_{\mathrm{S},2} \omega_{\mathrm{S},3}}{N_2 K_2 N_3 K_3} \tag{9}$$

$$m_{\mathrm{III}} = \frac{\omega_{\mathrm{L},1} \omega_{\mathrm{L},2}}{N_1 K_1} \tag{10}$$

$$m_{\mathrm{IV}} = \omega_{\mathrm{L},1} \tag{11}$$

These parameters are expressed in function of four unknown ω parameters of the system. The application of the omega rules to zones II, III and to the feed node, gives Eqs. (12) and (13):

$$\omega_{\mathrm{L},1} = \omega_{\mathrm{S},1} \tag{12}$$

$$\omega_{\mathrm{L},2} = \omega_{\mathrm{S},2} = \omega_{\mathrm{F},2} \tag{13}$$

In order to express the remaining variables in function of known parameters, mass balance equations can be written for every compound on the feed node (14) and on interfaces I1 and I2 (15).

$$m_{\mathrm{F}} C_{\mathrm{F},i} + m_{\mathrm{II}} C_{\mathrm{LII},i} = m_{\mathrm{III}} C_{\mathrm{L},i}, \quad \forall i \in [1,3] \tag{14}$$

$$m_{\mathrm{zone}} = \frac{n_{\mathrm{S},i} - n_{\mathrm{zone},i}}{C_{\mathrm{L\ or\ LII},i} - C_{\mathrm{zone},i}}, \quad \forall i \in [1,3], \text{ zone} = \mathrm{II}, \mathrm{III}. \tag{15}$$

By substituting Eqs. (6), (7), (9) and (10) into Eqs. (14) and (15), Eqs. (16)–(18) can be reached after simplifications:

$$m_{\mathrm{F}} C_{\mathrm{F},1} = N_1 \cdot \left(\frac{\omega_{\mathrm{F},2}}{N_1 K_1} - 1\right)\left(1 - \frac{\omega_{\mathrm{S},1}}{N_1 K_1}\right) \tag{16}$$

$$m_{\mathrm{F}} C_{\mathrm{F},2} = N_2 \cdot \frac{N_2 K_2 - N_1 K_1}{N_2 K_2 - N_3 K_3} \cdot \left(1 - \frac{\omega_{\mathrm{F},2}}{N_2 K_2}\right)\left(1 - \frac{\omega_{\mathrm{S},3}}{N_2 K_2}\right) \tag{17}$$

$$m_{\mathrm{F}} C_{\mathrm{F},3} = N_3 \cdot \frac{N_3 K_3 - N_1 K_1}{N_3 K_3 - N_2 K_2} \cdot \left(1 - \frac{\omega_{\mathrm{F},2}}{N_3 K_3}\right)\left(1 - \frac{\omega_{\mathrm{S},3}}{N_3 K_3}\right). \tag{18}$$

The elimination of the variable $\omega_{\mathrm{S},3}$ in Eqs. (17) and (18) leads to Eq. (19), which gives the expression of the feed flow-rate ratio for a ternary TMB working at the LSC point (case KEY=1):

$$\frac{1}{m_F} = \frac{C_{F,2}/N_2}{\left(1-\frac{\omega_{F,2}}{N_2K_2}\right)\cdot\left(1-\frac{N_1K_1}{N_2K_2}\right)} + \frac{C_{F,3}/N_3}{\left(1-\frac{\omega_{F,2}}{N_3K_3}\right)\cdot\left(1-\frac{N_1K_1}{N_3K_3}\right)} \quad (19)$$

This equation is expressed only in function of feed and retention parameters and can consequently be calculated for any given separation. In order to characterize entirely the system, the value of parameters $\omega_{S,1}$, $\omega_{S,3}$ can be determined by using Eqs. (16)–(18), which results in Eqs. (20) and (21):

$$\omega_{S,1} = N_1K_1\cdot\left(1-\frac{m_F\cdot C_{F,1}\cdot K_1}{\omega_{F,2}-N_1K_1}\right) \quad (20)$$

$$\omega_{S,3} = N_2K_2 \cdot\left[1-m_FC_{F,2}\cdot\left(\frac{N_2K_2-N_3K_3}{N_2K_2-N_1K_1}\right)\cdot\left(\frac{K_2}{N_2K_2-\omega_{F,2}}\right)\right] \quad (21)$$

Submitting Eqs. (20) and (21) into Eqs. (9)–(11) gives the expressions of the flow-rate ratios in function of known parameters:

$$m_{II} = \frac{N_1K_1\omega_{F,2}}{N_3K_3} \cdot\left[1-m_FC_{F,2}\cdot\left(\frac{N_2K_2-N_3K_3}{N_2K_2-N_1K_1}\right)\cdot\left(\frac{K_2}{N_2K_2-\omega_{F,2}}\right)\right] \quad (22)$$

$$m_{III} = \omega_{F,2}\cdot\left(1-\frac{m_FC_{F,1}K_1}{\omega_{F,2}-N_1K_1}\right) \quad (23)$$

$$m_{IV} = N_1K_1\cdot\left(1-\frac{m_FC_{F,1}K_1}{\omega_{F,2}-N_1K_1}\right) \quad (24)$$

The first ternary four-zone TMB is entirely defined at the LSC point and all the working flow-rate ratios m have an analytical expression only function of known feed and retention parameters.

CASE KEY 2

The right concentration state has to be stabilized in every zone to get purified products in the required stream. Applying the results from Table 1 with KEY=2 and $M=3$ at the LSC point requires the choice of the highest border value for m_{III}, and m_{IV} and the lowest one for m_I, and m_{II} which results into Eqs. (8) and (11), respectively, for m_I and m_{IV}, and Eqs. (25) and (26) for, respectively, m_{II} and m_{III}:

$$m_{II} = \frac{N_2K_2\omega_{S,3}}{N_3K_3} \quad (25)$$

$$m_{III} = \frac{\omega_{L,1}\omega_{L,2}\omega_{L,3}}{N_1K_1N_2K_2}. \quad (26)$$

These parameters are expressed in function of four unknown ω parameters. Applying the omega rules to zones II, III and to the feed node leads to relationships (27)–(29).

$$\omega_{S,3} = \omega_{L,3} = \omega_{F,3} \quad (27)$$

$$\omega_{S,1} = \omega_{L,1} \quad (28)$$

$$\omega_{S,2} = \omega_{L,2} \quad (29)$$

The mass balance Eqs. (14) and (15) can be written by using Eqs. (6), (7), (25) and (26) which leads to Eqs. (30)–(32):

$$m_FC_{F,1} = N_1\cdot\frac{N_1K_1}{N_1K_1-N_2K_2}\cdot\prod_{j=1}^{3}\left(\frac{\omega_{S,j}}{N_1K_1}-1\right) \quad (30)$$

$$m_FC_{F,2} = N_2\cdot\frac{N_2K_2}{N_2K_2-N_1K_1}\cdot\prod_{j=1}^{3}\left(\frac{\omega_{S,j}}{N_2K_2}-1\right) \quad (31)$$

$$m_FC_{F,3} = N_3\cdot\left(1-\frac{N_2K_2}{N_3K_3}\right)\cdot\left(1-\frac{\omega_{F,3}}{N_3K_3}\right) \quad (32)$$

Eq. (32) gives the expression of the feed flow-rate ratio in function of known parameters.

Moreover, Eqs. (30) and (31) can be used to get analytical expression of the parameters $\omega_{S,1}$ and $\omega_{S,2}$:

$$\omega_{S,1}+\omega_{S,2} = N_1K_1\cdot\left(1-m_FC_{F,1}\cdot\frac{K_1}{\omega_{F,3}-N_1K_1}\right) + N_2K_2\left(1-m_FC_{F,2}\cdot\frac{K_2}{\omega_{F,3}-N_2K_2}\right) \quad (33)$$

$$\omega_{S,1}\omega_{S,2} = N_1K_1N_2K_2 \cdot\left(1 - m_F C_{F,1}\cdot\frac{K_1}{\omega_{F,3} - N_1K_1} - m_F C_{F,1}\cdot\frac{K_2}{\omega_{F,3} - N_2K_2}\right) \quad (34)$$

Finally, the flow-rate ratios in every zone of a four-zone TMB processing a ternary mixture at the LSC point (case KEY=2) are obtained by substituting Eqs. (33) and (34) into Eqs. (11), (25) and (26):

$$m_{II} = \frac{N_2K_2\omega_{F,3}}{N_3K_3} \quad (35)$$

$$m_{III} = \omega_{F,3}\cdot\left[1 - m_F C_{F,1}\cdot\left(\frac{K_1}{\omega_{F,3} - N_1K_1} - \frac{K_2}{\omega_{F,3} - N_2K_2}\right)\right] \quad (36)$$

$$m_{IV} = \omega_{S,1} \quad (37)$$

As far as zone I is concerned, Eq (8) is used. We can consider that the first ternary four-zone TMB (case KEY=2) is entirely defined at the LSC point and all the working flow-rate ratios m have an analytical expression function of known feed and retention parameters.

2.4. Second four zones TMB (binary mixture)

After having defined entirely both ternary four-zone TMB (cases KEY=1 and KEY=2) at the LSC point, a binary four-zone TMB is added to fractionate the two non-separated compounds produced by either the extract or the raffinate stream. The corresponding stream is supposed to be sent continuously to the second TMB. Consequently, this stream corresponds to the feed stream of the second TMB and as all the flow-rate ratios of the first TMB are known, it is possible to write a mass balance equation on the two involved compounds in order to know the feed concentrations of the second TMB. Therefore these feed concentrations are considered to be known as well as the value of their corresponding ω parameters obtained by solving the characteristic Eq. (3). The binary mixture is represented by A and B, with A being the less retained compound. The following relations can be applied depending on the case of study: Case KEY=1, A=2 and B=3 or Case KEY=2, A=1 and B=2. The complete results of this configuration with the hypotheses initially assumed are given by Mazzotti et al. [13] and we will briefly recall them at this point.

The application of the waves stabilization rule, corresponds to the application of M=2 in the results summarized in Table 1, which leads to Eq. (38).

$$m_I = N_BK_B,\quad m_{II} = \frac{N_AK_A\omega_{S,B}}{N_BK_B},\quad m_{III} = \frac{\omega_{L,A}\omega_{L,B}}{N_AK_A},\quad m_{IV} = \omega_{L,A} \quad (38)$$

The use of the omega rules and the resolution of the mass balance equations system obtained from the application of the equilibrium theory to a four-zone TMB processing a binary mixture result in the Eq. (39):

$$\omega_{L,B} = \omega_{S,B} = \omega_{F,B} \quad \text{and} \quad \omega_{L,A} = \omega_{S,A} = \omega_{F,A}\cdot\left[1 + \frac{(N_AK_A/\omega_{F,A} - 1)^2}{N_BK_B/\omega_{F,A} - 1}\right] \quad (39)$$

These relations can be used to obtain the expression in function of known parameters of all the working flow-rate ratios m of a TMB processing a binary mixture at the LSC point:

$$m_I = N_BK_B \quad (40)$$

$$m_{II} = \frac{N_AK_A\omega_{F,B}}{N_BK_B} \quad (41)$$

$$m_{III} = \frac{\omega_{F,A}\omega_{F,B}}{N_AK_A}\cdot\left[1 + \frac{(N_AK_A/\omega_{F,A} - 1)^2}{N_BK_B/\omega_{F,A} - 1}\right] \quad (42)$$

$$m_{IV} = \omega_{F,A}\cdot\left[1 + \frac{(N_AK_A/\omega_{F,A} - 1)^2}{N_BK_B/\omega_{F,A} - 1}\right] \quad (43)$$

It is also possible to get the expression of the feed flow-rate ratio of the second TMB by using Eqs. (42) and (43):

$$m_F = \frac{\omega_{F,A}\omega_{F,B}}{N_AK_AN_BK_B}\cdot\frac{(N_BK_B - N_AK_A)^2}{(N_BK_B - \omega_{F,A})} \quad (44)$$

These expressions allow us to conclude that the two four-zone TMB in a row at the LSC point are entirely characterized in function of the feed and retention parameters of the first TMB.

2.5. Solid flow-rate relationships

The two four-zone TMB are working continuously in a row, which means that the liquid stream produced by the first TMB containing the two non-separated compounds is sent to the second TMB and the value of the outlet liquid flow-rate of the first TMB becomes the feed flow-rate of the second TMB.

$$\text{Case KEY} = 1: Q_{\text{E}}^{(1)} = Q_{\text{F}}^{(2)} \tag{45}$$

$$\text{Case KEY} = 2: Q_{\text{R}}^{(1)} = Q_{\text{F}}^{(2)} \tag{46}$$

One can express the flow-rates in function of the flow-rate ratios and the solid flow-rate, which leads to Eqs. (47) and (48):

$$\text{Case KEY} = 1: \frac{Q_{\text{S}}^{(1)}}{Q_{\text{S}}^{(2)}} = \frac{m_{\text{F}}^{(2)}}{m_{\text{E}}^{(1)}} \tag{47}$$

$$\text{Case KEY} = 2: \frac{Q_{\text{S}}^{(1)}}{Q_{\text{S}}^{(2)}} = \frac{m_{\text{F}}^{(2)}}{m_{\text{R}}^{(1)}} \tag{48}$$

.

By reporting, respectively, for case KEY=1 and KEY=2 Eqs. (8), (22) and (44), and (36), (37) and (44) into Eqs. (47) and (48), one can reach the expressions of the relationship between the solid flow-rates involved in the 4+4-zone TMB configurations at the LSC point:

$$\text{Case KEY} = 1: \frac{Q_{\text{S}}^{(1)}}{Q_{\text{S}}^{(2)}} = \frac{\dfrac{\omega_{\text{E1,2}}\omega_{\text{E1,3}}(N_3K_3 - N_2K_2)^2}{N_2K_2N_3K_3(N_3K_3 - \omega_{\text{E1,2}})}}{\left(N_3K_3 - \dfrac{N_2K_2\omega_{\text{F,3}}}{N_3K_3}\right)} \tag{49}$$

$$\text{Case KEY} = 2: \frac{Q_{\text{S}}^{(1)}}{Q_{\text{S}}^{(2)}} = \frac{\dfrac{\omega_{\text{R1,1}}\omega_{\text{R1,2}}(N_2K_2 - N_1K_1)^2}{N_1K_1N_2K_2(N_2K_2 - \omega_{\text{R1,1}})}}{\left(\dfrac{\omega_{\text{S,1}}\cdot\omega_{\text{S,2}}\cdot\omega_{\text{F,3}}}{N_1K_1N_2K_2} - \omega_{\text{S,1}}\right)} \tag{50}$$

As said in the second four-zone TMB (binary mixture) part, the concentrations sent to the second TMB can be calculated by writing a mass balance equation on the two involved compounds between the feed and the sent stream. Moreover the corresponding ω variables sent to the second TMB can be determined by resolving the characteristic Eq. (3). Eqs. (49) and (50) complete the determination of the working flow-rates of the 4+4-zone TMB configurations.

2.6. Five-zone TMB followed by a four-zone TMB

In this process, the main difference with the previous one is based upon the use of a five-zone TMB in the first pass. In fact, this process is a classical four-zone TMB with one additional outlet stream being either a raffinate or an extract one. It means that this new production stream can be added either before or after the feed stream. These two configurations correspond to the two possible cases for the KEY compound. In other words, the five-zone TMB process will have one raffinate and two extracts or two raffinates and one extract for, respectively, KEY=1 or KEY=2. (Fig. 2). The application of the equilibrium theory to the two surrounding feed zones remains exactly the same as in the four-zone TMB case. In other words, for a given feed and retention data, the feed surrounding zones parameters (ω variables and flow-rate ratios m) remain exactly the same as the ones obtained for the four-zone TMB (cases KEY=l or 2). This result is due to the fact that the concentration waves of the system are generated at the feed node. Moreover, as no leakage of compounds is allowed through the liquid and solid recycling streams, there is no waves interference. Consequently, as the feed surrounding zones have the same utility in the four-zone TMB case as in the

Table 2
Five-zone TMB (case KEY=1) working flow-rate ratio intervals

Zone	Flow-rate ratio interval
I	$m_{\mathrm{I}} \geq N_3K_3$
II	$\frac{N_2K_2\omega_{\mathrm{E1S,3}}}{N_3K_3} \leq m_{\mathrm{II}} \leq \frac{\omega^2_{\mathrm{E1S,3}}}{N_3K_3}$
III	$\frac{N_1K_1\omega_{\mathrm{S,2}}\omega_{\mathrm{S,3}}}{N_2K_2N_3K_3} \leq m_{\mathrm{III}} \leq \frac{\omega_{\mathrm{S,1}}\omega_{\mathrm{S,2}}\omega_{\mathrm{S,3}}}{N_1K_1N_2K_2}$
IV	$\omega_{\mathrm{L,1}} \leq m_{\mathrm{IV}} \leq \frac{\omega_{\mathrm{L,1}}\omega_{\mathrm{L,2}}}{N_1K_1}$
V	$m_{\mathrm{V}} \leq \omega_{\mathrm{L,1}}$

five-zone TMB case, the flow-rate ratio m_{F} remains the same as the one obtained for the corresponding four-zone TMB process. Finally, the complete study of a five-zone TMB process means the application of the equilibrium theory to the remaining zones based upon the correct stabilization of the waves generated in the feed area. These results are summarized in Tables 2 and 3, respectively, for the cases KEY=1 and KEY=2 for a five-zone TMB processing a ternary mixture.

CASE KEY=1

In that particular case, the difficulty comes from zone II which is the extra zone added to the classical four-zone TMB process. In fact in this particular zone the inlet solid stream, containing compounds 2 and 3, and characterized by variables: $\omega_{\mathrm{E1S,2}}$, $\omega_{\mathrm{E1S,3}}$ generates two dispersive waves separating three concentration states in the following order: State 1, ($\omega_{\mathrm{E1S,2}}$, $\omega_{\mathrm{E1S,3}}$) | wave 1 |; State 2, (N_2K_2, $\omega_{\mathrm{E1S,3}}$) | wave 2 |; State 3, (N_2K_2, N_3K_3). To produce compounds 2 and 3 in the required streams, one has to stabilize state 2 inside zone II, which corresponds to the working interval summarized in Table 2. Our study is based upon the LSC point. This means that we have to choose m_{II} to maximize the ratio R, which can be expressed by Eq. (51):

$$R = (m_{\mathrm{IV}} - m_{\mathrm{III}})/(m_{\mathrm{I}} - m_{\mathrm{V}}) \tag{51}$$

The variable m_{II} is not involved in this definition, and it is not possible to choose the border value, which leads to the LSC point for this process alone. In fact, the second TMB process has to be added and the total eluent flow-rate Eq. (52), obtained by considering that the extract 1 stream is sent continuously to the second TMB, has to be considered.

$$Q_{\mathrm{E1}}^{(1)+(2)} = Q_{\mathrm{S}}^{(1)}\left[\left(m_{\mathrm{I}}^{(1)} - m_{\mathrm{V}}^{(1)}\right) + \left(m_{\mathrm{I}}^{(2)} - m_{\mathrm{IV}}^{(2)}\right)\frac{m_{\mathrm{II}}^{(1)} - m_{\mathrm{III}}^{(1)}}{m_{\mathrm{III}}^{(2)} - m_{\mathrm{II}}^{(2)}}\right] \tag{52}$$

In order to minimize its value, the lower border value of m_{II} of the first TMB has to be taken into account. Consequently the value of m_{II} is given by Eq. (53):

$$m_{\mathrm{II}} = \frac{N_2K_2\omega_{\mathrm{E1S,3}}}{N_3K_3} \tag{53}$$

This expression depends on variable $\omega_{\mathrm{E1S,3}}$, which can be linked to known variables by applying the omega rules to zones II and III:

$$\omega_{\mathrm{E1},i} = \omega_{\mathrm{E1S},i}, \quad i = 2,3 \tag{54}$$

$$\omega_{\mathrm{E1,3}} = \omega_{\mathrm{S,3}} \tag{55}$$

In fact, the flow-rate ratios of the five-zone TMB process have been determined at the LSC point. However, the concentration of compound 3 in the extract 1 stream cannot be calculated from a simple mass balance between the feed and extract 1 stream

Table 3
Five-zone TMB (case KEY=2) working flow-rate ratios intervals

Zone	Flow-rate ratio interval
I	$m_{\mathrm{I}} \geq N_3K_3$
II	$\frac{N_2K_2\omega_{\mathrm{S,3}}}{N_3K_3} \leq m_{\mathrm{II}} \leq \frac{\omega^2_{\mathrm{S,3}}}{N_3K_3}$
II	$\frac{\omega_{\mathrm{L,1}}\omega_{\mathrm{L,2}}}{N_1K_1} \leq m_{\mathrm{III}} \leq \frac{\omega_{\mathrm{L,1}}\omega_{\mathrm{L,2}}\omega_{\mathrm{L,3}}}{N_1K_1N_2K_2}$
IV	$\omega_{\mathrm{L,1}} \leq m_{\mathrm{IV}} \leq \frac{\omega_{\mathrm{R2,1}}\omega_{\mathrm{R2,2}}}{N_1K_1}$
V	$m_{\mathrm{V}} \leq \omega_{\mathrm{R1,1}}$

because it is produced in extracts 1 and 2. Thus, $C_{E1,3}$ has to be determined. In order to do so Eq. (6) can be applied to express $C_{E1,3}$ in function of $\omega_{E1,2}$ and $\omega_{E1,3}$. As $\omega_{E1,3}$ is known, $\omega_{E1,2}$ has to be determined. A mass balance equation on compound 2 between the feed and extract 1 stream is written:

$$(m_{II} - m_{III}) \cdot C_{E1,2} = (m_{III} - m_{IV}) \cdot C_{F,2} \quad (56)$$

by substituting Eqs. (6), (23), (24) and (53) one can reach Eq. (57) after simplifications:

$$\omega_{E1,2} = \frac{(N_2K_2)^2 - N_1K_1\omega_{F,2}}{2N_2K_2 - N_1K_1 - \omega_{F,2}} \quad (57)$$

These expressions result in the complete determination of the working flow-rates of the five-zone TMB and of the concentrations of compounds 2 and 3 sent to the second TMB at the LSC point:

CASE KEY=2

On contrary to the former case, the main difference with the equivalent four-zone TMB comes from the fourth zone which has been added. As said before, zones II and III have been fully characterized by the four-zone TMB study. In fact, the liquid stream entering zone IV contains two compounds and consequently generates two shock waves separating three concentration states, which are ordered as follows: State 3, ($\omega_{R2,1}$, $\omega_{R2,2}$) | wave 2 | State 2, ($\omega_{R2,1}$, N_2K_2) | wave 1 | State 1, (N_1K_1, N_2K_2).

As only compound 1 is required to be produced in raffinate 1, the concentration state 2 has to be stabilized into zone IV, which leads to the working intervals shown in Table 3 corresponding to the stabilization of wave 1 or wave 2. This work is based upon the LSC point which means that m_{IV} has to be maximized to minimize the total eluent flow-rate of the 5+4-zone TMB configuration as seen in Eq. (58):

$$Q_{E1}^{(1)+(2)} = Q_S^{(1)} \cdot \left[\left(m_I^{(1)} - m_V^{(1)}\right) + \left(m_I^{(2)} - m_{IV}^{(2)}\right) \cdot \frac{m_{III}^{(1)} - m_{IV}^{(1)}}{m_{III}^{(2)} - m_{II}^{(2)}} \right] \quad (58)$$

This leads to the following expressions of the flow-rate ratios m of the five-zone TMB process (case KEY=2):

$$m_{II} = \frac{N_2K_2\omega_{S,3}}{N_3K_3} \quad (59)$$

$$m_{III} = \frac{\omega_{L,1}\omega_{L,2}\omega_{L,3}}{N_1K_1N_2K_2}. \quad (60)$$

$$m_{IV} = \frac{\omega_{R2,1}\omega_{R2,2}}{N_1K_1} \quad (61)$$

$$m_V = \omega_{R1,1} \quad (62)$$

Eq. (8) can be considered for the flow-rate ratio in zone I. The ω variables of streams S and L have been calculated in the case of a four-zone TMB. To determine the value of the remaining unknown ω variables, the omega rules can be applied to zones III and IV of the five-zone TMB working at the LSC point:

$$\omega_{L,1} = \omega_{R2,1} = \omega_{R1,1} \quad (63)$$

$$\omega_{L,2} = \omega_{R2,2} \quad (64)$$

As a result, all the ω variables are determined in function of the known ω variables of the L liquid stream and the five-zone TMB is entirely characterized at the LSC point.

2.7. Second binary four-zone TMB

The application of a second binary four-zone TMB to process the two remaining non-separated compounds is based upon the knowledge of the two ω variables of the incoming liquid stream. This task has been performed previously for the different working cases (KEY=1 or KEY=2). Consequently, the results presented in the second four-zone TMB (binary case) can be applied. This leads to the complete characterization of the 5+4-zone TMB process.

2.8. Eight-zone TMB

The eight-zone TMB configurations correspond to the addition of the two four-zone TMB processes in

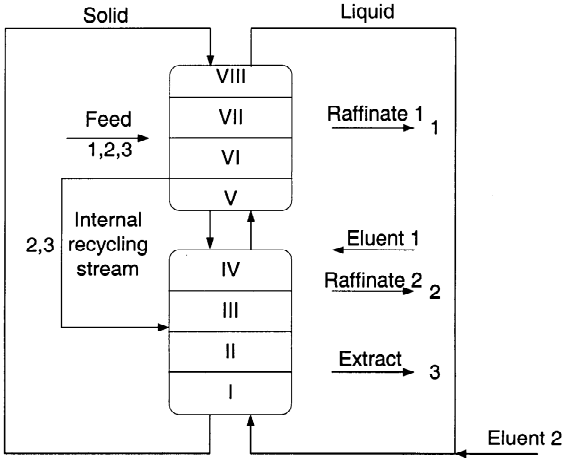

Fig. 8. Eight-zone TMB (Case KEY=1).

one device with the application of one solid flow-rate as illustrated in Fig. 8 for case KEY=1. The problem comes from the internal recycling stream. By applying a mass balance equation on this stream, one can reach Eqs. (65) and (66):

$$\text{Case KEY} = 1: m_{\text{int}} = \frac{Q_{\text{int}}}{Q_S} = m_V - m_{VI} = m_{III} - m_{II} \quad (65)$$

$$\text{Case KEY} = 2: m_{\text{int}} = \frac{Q_{\text{int}}}{Q_S} = m_{III} - m_{IV} = m_{VII} - m_{VI} \quad (66)$$

In the first place, the influence of these constraints on the determination of the working flow-rate is studied for case KEY=1. In fact, Eq. (65) has to be fulfilled continuously during all the process in order not to have any accumulation in the system. Nevertheless, this relation should be compatible with the initial goal, which is the production of pure compounds 1–3 in their specific streams. The methodology is based upon the triangular working regions in diagrams (m_{VI}, m_{VII}) and (m_{II}, m_{III}) schematized in Fig. 9. In order to know if the eight-zone TMB can work, the first four-zone TMB process (zones V–VIII) is entirely characterized at one given point. If one chooses the LSC point, all the calculations

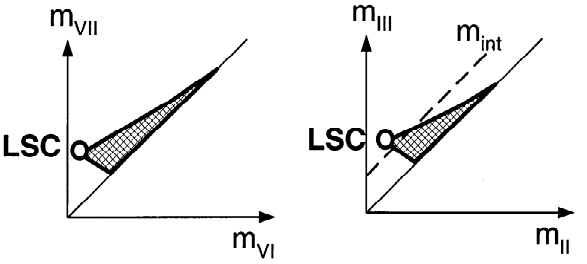

Fig. 9. Schematic working diagrams of the eight-zone TMB (case KEY=1).

presented previously can be used. If one wants to work with another point, the triangular working region of diagram (m_{VI}, m_{VII}) has to be determined. This work is presented for cases KEY=1 and KEY=2 in Appendix A. After the working point has been chosen, the concentrations and the flow-rate ratio of the internal recycling stream are known. This allows the determination of the triangular working region in diagram (m_{II}, m_{III}) of the second TMB (zones I–IV). Moreover Eq. (65) defines a working line for m_{int} in diagram (m_{II}, m_{III}) as schematized in Fig. 9. The process can work only if the flow-rates ratios m_{II} and m_{III} lie into the triangular working region and fulfill Eq. (65) simultaneously. This means that the eight-zone TMB (case KEY=1) is feasible only if the dashed line knows an intersection with the triangle in diagram (m_{II}, m_{III}). This defines the feasibility condition of the process, which is expressed by Eq. (67):

$$\text{Case KEY} = 1: F = (m_{III} - m_{II})_{LSC} - (m_V - m_{VI}) \geq 0 \quad (67)$$

The application of the same reasoning to the eight-zone TMB (case KEY=2) leads to Eq. (68):

$$\text{Case KEY} = 2: F = (m_{VI} - m_{VII})_{LSC} - (m_{III} - m_{IV}) \geq 0 \quad (68)$$

In a first place, one has to check if the eight-zone TMB process (case KEY=1 or 2) can fractionate a ternary mixture at the LSC point, by using Eqs. (67) and (68). If this is the case, the working flow-rates of

the second TMB will be chosen inside the working segment defined by the intersection of the dashed line and the triangular region (Fig. 9). If this is not the case, there may exist a feed flow-rate different from the LSC point one, which could lead to a different conclusion. Obviously, this would be less interesting than the corresponding 4+4-zone TMB because it would process a smaller amount of compounds. However, it would be interesting to know if this process can work anyway. We will discuss this problem for both cases.

Case KEY=1

In the entire working region, we look for the maximum value of the feasibility condition F given by Eq. (67). The expressions of the flow-rate ratios $m_{\text{int}}$and $m_{F,\text{LSC}}$ involved in the feasibility condition (67) are given by Eqs. (69) and (70) by using Eq. (44):

$$m_{\text{int}} = m_{\text{V}} - m_{\text{VI}} \tag{69}$$

$$m_{F,\text{LSC}} = (m_{\text{III}} - m_{\text{II}})_{\text{LSC}} = \frac{\omega_{\text{int},2}\omega_{\text{int},3}(N_3K_3 - N_2K_2)^2}{N_2K_2N_3K_3(N_3K_3 - \omega_{\text{int},2})} \tag{70}$$

In fact the highest value of F is obtained when m_{int} is minimal and $m_{F,\text{LSC}}$ is maximal. In order to ensure the first condition, m_{VI} has to be maximized for a given flow-rate ratio m_{V} and this corresponds to the right part of the working triangle in diagram (m_{VI}, m_{VII}) (Fig. 9). To ensure the second condition, Eq. (70) shows that the ω variables have to be maximized. The higher border values are given by $\omega_{\text{int},2} = N_2K_2$ and $\omega_{\text{int},3} = N_3K_3$ from Eq. (5). In fact these values are reached for a zero feed flow-rate. Consequently, this corresponds to the extreme right point of the triangle. At this point, no component is present in zone VI, consequently the composition of the dispersive wave stabilized in zone VI is characterized by $\omega_2 = N_2K_2$ and $\omega_3 = N_3K_3$. The application of Eq. (9) to express m_{VI} leads to the fact that $m_{\text{int}} = m_{F,\text{LSC}} = N_3K_3 - N_2K_2$ at this point. This determines a working point for the eight-zone TMB (case KEY=1). In order to know if this is the only working point, the variation of F has to be studied along the right curve of the triangle (Fig. 9). In fact, when m_F increases, components 2 and 3 are sent to the second TMB with a concentration different from zero. As a result, the characteristic Eq. (3) leads to a $\omega_{\text{int},2} < N_2K_2$ and $\omega_{\text{int},3} < N_3K_3$. Eq. (70) shows that $m_{F,\text{LSC}}$ has a lower value than the one obtained for the upper right point. As far as m_{VI} is concerned, if m_F lies under $m_{F,C}$, it can be expressed by Eq. (9) for a given composition (ω_2, ω_3) stabilized in zone VI. As m_F is different from zero, relations (71) are fulfilled:

$$\omega_2 < N_2K_2, \omega_3 < N_3K_3 \tag{71}$$

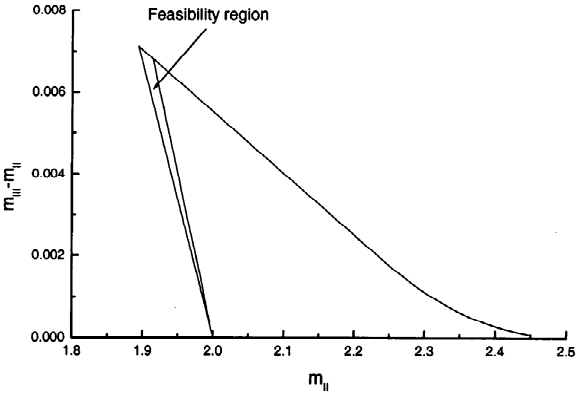

Fig. 10. Region of feasibility of the eight zones TMB (Case KEY=2) on example 1.

Table 4
Numerical examples

	Example 1			Example 2			Example 3			Example 4		
Compounds:	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
N (g/l)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
K (L/g)	1.0	2.0	2.5	1.2	1.9	4.0	1.0	2.45	2.5	1.05	1.1	2.5
C_F (g/l)	0.5	5.0	1.5	2.0	0.1	0.3	0.5	2.0	1.0	0.7	1.0	0.5

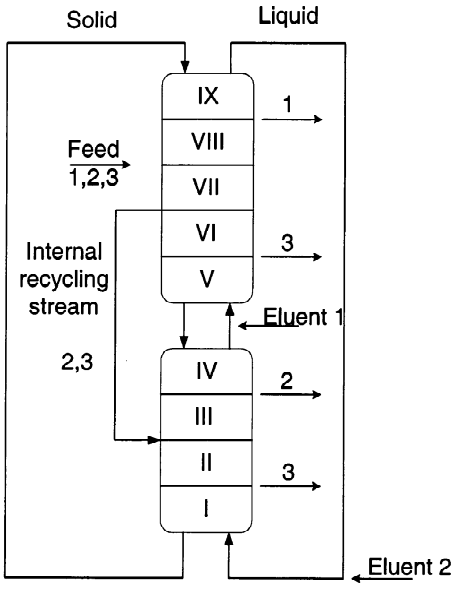

Fig. 11. Nine-zone TMB process (case KEY=1).

Consequently, F has a value lower than zero for the right curve under the critical point. Moreover, if m_F is greater than $m_{F,C}$, one can see on Eqs. (A.7), (A.13) and (A.14) that m_{VI}, decreases, which shows that m_{int} increases also. Consequently F decreases on the right curve above the critical point. Consequently, this discussion demonstrates that the eight-zone TMB (case KEY=1) is feasible only at the upper right point of the triangle because this is the maximum value of the feasibility condition F. Unfortunately, this corresponds to a zero feed flow-rate, and this point does not correspond to a practical working point.

Case KEY=2

In some cases the eight-zone TMB process was able to process a ternary mixture for a feed flow-rate different from zero. Numerical example 1 summarized in Table 4 is considered and Fig. 10 shows the region of feasibility, which has been plotted in diagram (m_{II}, $m_{III}-m_{II}$). As a conclusion, it has been demonstrated that the eight-zone TMB (case KEY=1) is not able to process a ternary mixture into three pure fractions. As far as the eight-zone TMB (case KEY=2) is concerned, there exists examples, which are able to process a ternary mixture at the LSC point and this has been shown on a given numerical example.

2.9. Nine-zone TMB

This process corresponds to the addition of the five-zone to the four-zone TMB into one single device characterized by a unique solid flow-rate and an internal recycling stream working continuously as can be seen on Fig. 11 for case KEY=1. As for the eight-zone TMB process, these two constraints lead to a feasibility condition. This condition has to be checked in order to know if the process can produce three pure compounds where required. As a result, the methodology to be applied consists in determining the working flow-rates of the five-zone TMB as well as the recycling concentrations at a given working point, and check the feasibility condition at this particular point. The determination of the five-zone TMB begins at the LSC point, which has already been explained, and then if the feasibility condition is not verified, one has to explore the triangular working region corresponding to the feed surrounding zones working intervals. As a matter of

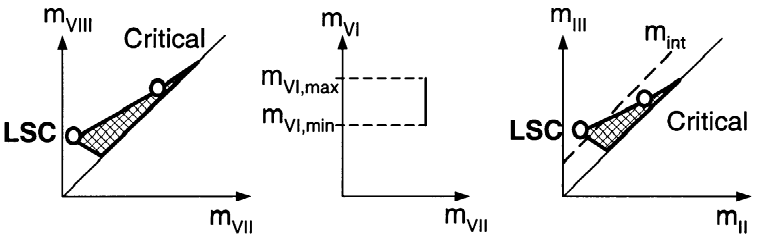

Fig. 12. Working methodology for a nine-zone TMB (case KEY=1).

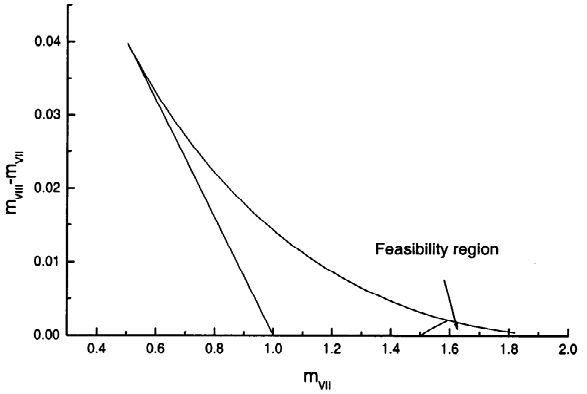

Fig. 13. Region of feasibility of the nine-zone TMB (Case KEY=1) on example 1.

fact, the determination of this region has been explained in Appendix A for cases KEY=1 and 2. However, one additional zone has to be considered in comparison to the eight-zone TMB. It is then possible to check in the entire triangular feed working region if there exists any possible working point for which the production goal is reached. Fig. 12 illustrates the methodology to be applied at the LSC point for the nine-zone TMB (case KEY=1). In fact one working point in diagram (m_{VII}, m_{VIII}) is chosen, as well as a corresponding flow-rate ratio in zone VI.

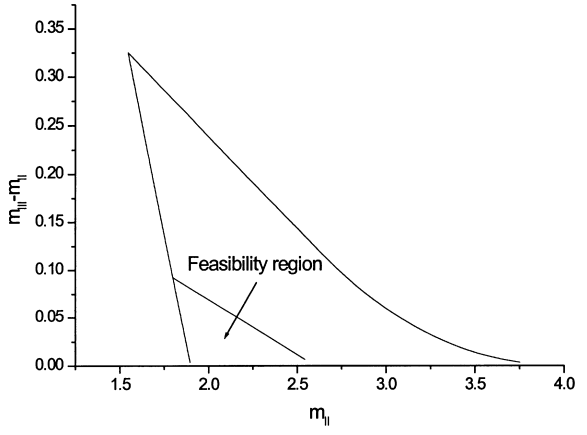

Fig. 14. Region of feasibility of the nine-zone TMB (Case KEY=2) on example 2.

Then the feasibility condition is checked on diagram (m_{II}, m_{III}) corresponding to the fact that the internal recycling dashed line has to cross the triangular region in order to define a working segment. In order to obtain an expression of the feasibility condition, a mass balance equation on the recycling stream can be written to link all the four different working flow-rates involved:

$$\text{Case KEY} = 1 \; m_{\text{int}} = m_{\text{VI}} - m_{\text{VII}} = m_{\text{III}} - m_{\text{II}} \quad (72)$$

$$\text{Case KEY} = 2 \; m_{\text{int}} = m_{\text{III}} - m_{\text{IV}} = m_{\text{VIII}} - m_{\text{VII}} \quad (73)$$

As already explained for the eight-zone TMB, the feasibility condition can be expressed as follows:

$$\text{Case KEY} = 1 \; F = (m_{\text{III}} - m_{\text{II}})_{\text{LSC}} - (m_{\text{VI}} - m_{\text{VII}}) \geq 0 \quad (74)$$

$$\text{Case KEY} = 2 \; F = (m_{\text{VIII}} - m_{\text{VII}})_{\text{LSC}} - (m_{\text{III}} - m_{\text{IV}}) \geq 0 \quad (75)$$

Depending on the feed and retention parameters, the nine-zone TMB process could produce three pure compounds at the LSC point or at another working point or was even not able to process the considered ternary mixture. On numerical example 1 given in Table 4, the nine-zone TMB (Case KEY=1) can process the ternary mixture at a point different from the LSC point as seen on Fig. 13, and the nine-zone TMB (Case KEY=2) works at the LSC point and in the entire triangular working region. On numerical example 2 given in Table 4, the nine-zone TMB (Case KEY=1) can work at the LSC point and in the entire triangular region, and the nine-zone TMB (Case KEY=2) can work at a point different from the LSC point as illustrated in Fig. 14. Finally the nine-zone TMB (Case KEY=l and KEY=2) cannot, respectively, fractionate the mixture of numerical examples 3 and 4 given in Table 4. Consequently, depending on the case studied, one has to determine carefully the feasibility condition and check if the

Table 5
Feed and eluent flow-rates at the LSC point (Case KEY=1)

TMB	Q_F	Q_S^1	Q_S^2	Q_{E1}^1	Q_{E1}^2	ΣQ_{E1}	R
4+4	0.0930	1.0	0.694	3.211	1.466	4.677	0.020
5+4	0.0930	1.0	0.366	3.211	0.787	3.998	0.023
8 zones	No solution						
9 zones	0.0930	1.0	1.0	3.211	2.117	5.328	0.017

nine-zone TMB can fractionate the considered mixture. If this is not possible at the LSC point, the feed flow-rate ratio will be lower than the one observed for the two devices TMB (4+4 and 5+4). This means that the nine-zone TMB will work in conditions less interesting than the other configurations.

3. Configurations comparison

The objective of this work consists in the application of the equilibrium theory to different ternary TMB in order to determine their corresponding working flow-rate ratios. As a matter of fact, this application results in many possible working points, and among all of them, the LSC point defined as the one giving the highest value of the ratio R has been chosen. As a result, the value obtained for all the configurations can be compared in order to know which configuration is more suitable. As a matter of fact, the expressions of the feed flow-rate ratio are, respectively, given by Eqs. (19) and (32) for cases KEY=1 and KEY=2 for all the configurations if they are working at the LSC point. The eight- and nine-zone TMB configurations may work for some examples depending on the feasibility condition. As far as the total eluent flow-rate expression is concerned, the flow-rate ratios of the zones involved in the eluent stream expression have to be used. In fact it is not possible to get simple expressions of the ratio R which can be compared in a general way and which would have given general rules to be applied to choose the best configuration for a given ternary mixture. It is possible though to calculate its value as soon as the values of the feed concentrations and the retention parameters are given. Consequently, numerical example 2 given in Table 4 is taken into account. The application of the equilibrium theory to all the configurations has been performed and the corresponding values of the feed and eluent flow-rates are given at the LSC point in Tables 5 and 6. These tables indicate that for this given numerical example, it is more suitable to use the 5+4-zone TMB (Case KEY=2) configuration because it shows the highest value of ratio R.

4. Conclusion

In conclusion, the overall methodology used to determine the working flow-rates of a TMB process has been given in the frame of the equilibrium theory for compounds characterized by langmuirian isotherms. This methodology has been used to de-

Table 6
Feed and eluent flow-rates at the LSC point (Case KEY=2)

TMB	Q_F	Q_S^1	Q_S^2	Q_{E1}^1	Q_{E1}^2	ΣQ_{E1}	R
4+4	0.325	1.0	4.8661	3.291	4.813	8.104	0.040
5+4	**0.325**	**1.0**	**3.3051**	**3.291**	**3.269**	**6.560**	**0.050**
8 zones	No solution						
9 zones	(solution ≠ LSC 0.0950)	1.0	1.0	2.975	0.940	3.915	0.024

termine the feed and eluent flow-rates of various TMB configurations (4+4-, 5+4-, eight- and nine-zone TMB) processing ternary mixtures at the LSC point. The complete characterization of the ternary and binary four- and five-zone TMB processes has been given, which allows the direct calculation of all the flow-rate values from the feed and retention parameters thanks to their analytical expressions. These expressions can be used to choose the best configuration to be applied for a given mixture, and this has been illustrated by an example. It has been demonstrated that the eight-zone TMB (case KEY= 1) cannot process a ternary mixture into three pure fractions simultaneously in our work frame. Moreover, the eight- and nine-zone configurations can process a ternary mixture as efficiently as the 4+4- and 5+4-zone TMB only if the entire process is working at the LSC point, which is satisfied only in very specific cases.

Finally, on a practical point of view, the previous results obtained in the frame of the equilibrium theory enable the first determination of the working flow-rates of a given ternary SMB process. This task is quite impossible to perform by a simple trial and error method. Moreover, the working regions may be used to understand the reasons why a given SMB experiment did not work properly, and change correctly the flow-rates values in order to get better performances.

5. Nomenclature

A	Less retained compound (binary mixtures)
B	More retained compound (binary mixtures)
1	Less retained compound (ternary mixtures)
2	Intermediary compound (ternary mixture)
3	More retained compound (ternary mixture)
C (g/l)	Concentration in the liquid phase
D	Langmuir isotherm expression denominator
F	Feasibility condition
K	Retention factor (L/g)
KEY	Compound KEY
m	Flow rates ratio ($=Q_{liquid}/I\ Q_{solid}$)
n	Concentration in the solid phase (g/l)
N	Saturation capacity (g/l)
Q (ml/min)	Flow rate
r	Feed ratio: $r=m_F/m_{F,LSC}$
R	Ratio Q_F/Q_{E1}
ω	Equilibrium theory parameter

Subscripts

C	Critical point
E1	Eluent
E	Extract stream
E1	Extract 1 stream
ES	Extract corresponding solid stream
E1S	Extract 1 corresponding solid stream
F	Feed
int	Internal recycling stream
I1, I2	Feed surrounding zone interfaces
L	Liquid stream following the feed inlet
LII	Liquid stream preceding the feed inlet
R	Raffinate stream
R1	Raffinate 1 stream
RS	Raffinate corresponding solid stream
R1S	Raffinate 1 corresponding solid stream
s	Solid stream
S	Solid stream corresponding to L stream
I–IX	zones

Superscripts

1	First TMB
2	Second TMB

Appendix A. Determination of the working region of a four-zone TMB processing a ternary mixture

The triangular working region of a four-zone TMB process (Fig. 1) schematized in Fig. 15 is determined for cases KEY=1 and 2.

CASE KEY=1

In order to determine the triangular region of this process, one has to consider zones II and III surrounding the feed stream (Fig. 7) and more especially the concentration states and waves generated inside each zone as schematized in Fig. 16. The

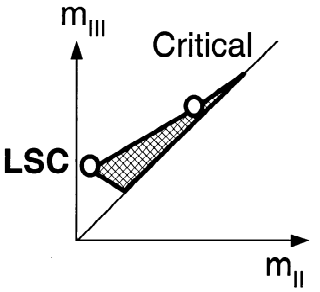

Fig. 15. Schematic triangular working region of four-zone TMB.

conditions of stabilization of the concentration states inside zones II and III summarized in Table 1 generate a triangular working region in diagram (m_{II}; m_{III}) as seen in Fig. 15. In fact for case KEY=1, one wants to produce compound 1 in the raffinate stream and compounds 2 and 3 in the extract stream. This corresponds to the stabilization of concentration state 2 in zone III and concentration state 2 in zone II. The LSC point corresponds to the stabilization of the end of dispersive wave 2 in zone II coupled with the stabilization of shock 2 in zone III. The left part of the triangle corresponds to the stabilization of the end of dispersive wave 2 in zone II. The right part corresponds to the stabilization of shock 2 in zone III. The critical point corresponds to the stabilization of the end of dispersive wave 2 in zone II coupled with the stabilization of shock 2 in zone III.

Left part of the triangle

A given value of the feed flow-rate ratio is considered: $m_F = r \cdot m_{F,LSC}$, $r < 1$. For this given value, the mass balance Eqs. (14) and (15) are written on compounds 2 and 3, which gives the system of Eqs. (A.1) and (A.2):

$$m_F C_{F,2} = N_2 \cdot \frac{N_2K_2 - N_1K_1}{N_2K_2 - N_3K_3} \cdot \left(1 - \frac{\omega_{S,2}}{N_2K_2}\right) \cdot \left(1 - \frac{\omega_{S,3}}{N_2K_2}\right) \quad (A.1)$$

$$m_F C_{F,3} = N_3 \cdot \frac{N_3K_3 - N_1K_1}{N_3K_3 - N_2K_2} \cdot \left(1 - \frac{\omega_{S,2}}{N_3K_3}\right) \cdot \left(1 - \frac{\omega_{S,3}}{N_3K_3}\right) \quad (A.2)$$

These equations are modified to reach Eqs. (A.3) and (A.4), which give the expression of the sum and product of the involved variables:

$$\omega_{S,2} + \omega_{S,3} = N_2K_2 \cdot \left(1 - \frac{K_2 r m_{F,LSC} C_{F,2}}{N_2K_2 - N_1K_1}\right) + N_3K_3 \cdot \left(1 - \frac{K_3 r m_{F,LSC} C_{F,3}}{N_3K_3 - N_1K_1}\right) \quad (A.3)$$

$$\omega_{S,2}\omega_{S,3} = N_2K_2N_3K_3 \cdot \left(1 - \frac{K_2 r m_{F,LSC} C_{F,2}}{N_2K_2 - N_1K_1} - \frac{K_3 r m_{F,LSC} C_{F,3}}{N_3K_3 - N_1K_1}\right). \quad (A.4)$$

These equations allow us to determine the value of the two involved ω variables. The flow-rate ratio m_{II} is minimal in this part of the triangle, so it can be expressed by Eq. (A.5), which is the lower border value shown in Table 1:

$$m_{II} = \frac{N_1K_1\omega_{S,2}\omega_{S,3}}{N_2K_2N_3K_3} \quad (A.5)$$

Substituting Eq. (A.4) into (A.5) gives Eq. (A.6).

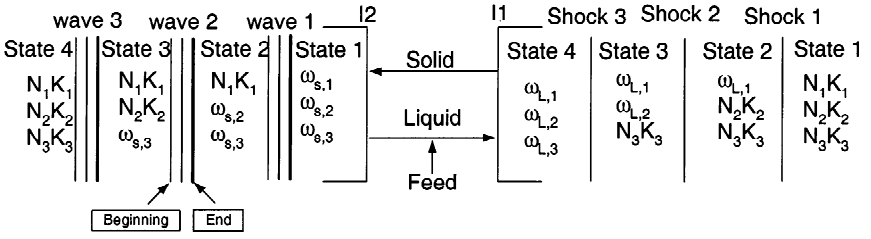

Fig. 16. States and waves generated in the feed surrounding zones.

$$m_{\mathrm{II}} = N_1 K_1 \cdot \left(1 - \frac{K_2 r m_{\mathrm{F,LSC}} C_{\mathrm{F},2}}{N_2 K_2 - N_1 K_1} - \frac{K_3 r m_{\mathrm{F,LSC}} C_{\mathrm{F},3}}{N_3 K_3 - N_1 K_1}\right) \tag{A.6}$$

This equation shows a linear variation of m_{II} with r, which tends to a value of $N_1 K_1$ if r tends to zero. The value of m_{III} can be reached by applying a simple mass balance equation on the feed node.

$$m_{\mathrm{III}} = m_{\mathrm{F}} + m_{\mathrm{II}} \tag{A.7}$$

Consequently, the left part of the triangle can be plotted in function of r with Eqs. (A.6) and (A.7). However, the complete characterization of the TMB process comes with the knowledge of all the ω variables. The remaining unknown variable $\omega_{\mathrm{S},1} = \omega_{\mathrm{L},1}$ can be determined by writing the mass balance Eqs. (14) and (15) of compound 1, which leads to Eq. (A.8):

$$r \cdot m_{\mathrm{F,LSC}} \cdot C_{\mathrm{F},1} = N_1 \cdot (m_{\mathrm{III}} - \omega_{\mathrm{S},1}) \cdot \left(\frac{1}{\omega_{\mathrm{S},1}} - \frac{1}{N_1 K_1}\right) \tag{A.8}$$

This equation can be expressed as a second-degree polynomial Eq. (A.9) of the sum and product of the two solutions:

$$\begin{aligned} \text{sum} &= m_{\mathrm{III}} + N_1 K_1 + K_1 r m_{\mathrm{F,LSC}} C_{\mathrm{F},1} \\ \text{product} &= m_{\mathrm{III}} N_1 K_1 \end{aligned} \tag{A.9}$$

The lowest solution will be chosen for $\omega_{\mathrm{S},1}$ in order to fulfill Eq. (5). The left part of the triangle is then entirely defined.

Right part of the triangle

First of all, the critical feed flow-rate ratio $m_{\mathrm{F},C}$ characterized by $r = r_C = m_{\mathrm{F},C}/m_{\mathrm{F,LSC}}$ has to be determined. On this specific point of the triangle, the application of the omega rules on zone II and III leads to $\omega_{\mathrm{S},2} = \omega_{\mathrm{F},2}$. Moreover, as m_{II} stabilizes the end of dispersive wave in zone II, its expression is given by Eq. (A.10):

$$m_{\mathrm{II}} = \frac{(\omega_{\mathrm{F},2})^2 \omega_{\mathrm{S},3}}{N_2 K_2 N_3 K_3} \tag{A.10}$$

The mass balance Eqs. (14) and (15) written on compounds 2 and 3, result into Eq. (A.11):

$$m_{\mathrm{F},C} \cdot C_{\mathrm{F},i} = n_i - m_2 \cdot C_i, \quad i = 2,3 \tag{A.11}$$

The critical flow-rate ratio expression (A.12) is obtained by substituting Eqs. (A.10), (1), (6) into (A.11):

$$\frac{1}{m_{\mathrm{F},C}} = \frac{C_{\mathrm{F},2}/N_2}{\left(1 - \frac{\omega_{\mathrm{F},2}}{N_2 K_2}\right)^2} + \frac{C_{\mathrm{F},3}/N_3}{\left(1 - \frac{\omega_{\mathrm{F},2}}{N_3 K_3}\right)^2} \tag{A.12}$$

After this, the determination of the right part of the triangle can be performed depending on the value of variable r:

$r > r_C$

In that case, the feed flow-rate ratio value is higher than the critical value and lower than the LSC point value. The application of the omega rules to zones II and III results in the relationship $\omega_{\mathrm{S},2} = \omega_{\mathrm{F},2}$. The flow-rate ratio m_{III} is maximal, and its expression is given by Eq. (A.13) corresponding to the higher border value shown in Table 1:

$$m_{\mathrm{III}} = \frac{\omega_{\mathrm{S},1} \omega_{\mathrm{F},2}}{N_1 K_1} \tag{A.13}$$

By using Eq. (A.13) into the mass balance Eqs. (14) and (15) written on compound 1, Eq. (A.14) is reached:

$$r m_{\mathrm{F,LSC}} C_{\mathrm{F},1} = N_1 \cdot \left(\frac{\omega_{\mathrm{F},2}}{N_1 K_1} - 1\right) \cdot \left(1 - \frac{\omega_{\mathrm{S},1}}{N_1 K_1}\right) \tag{A.14}$$

In fact, for a given feed flow-rate ratio, the value of m_{III} is obtained by replacing the expression of $\omega_{\mathrm{S},1}$ from Eq. (A.14) into Eq. (A.13). The value of m_{II} is obtained from Eq. (A.7). This results into a linear variation of m_{II} in function of r. The remaining unknown variable $\omega_{\mathrm{S},3}$ is obtained by solving the mass balance Eq. (A.15) written on compound 2:

$$r m_{\mathrm{F,LSC}} \cdot C_{\mathrm{F},2} = \left(\frac{\omega_{\mathrm{F},2} \omega_{\mathrm{S},2}}{N_3 K_3} - m_{\mathrm{II}}\right) \cdot \frac{1}{K_2} \cdot \frac{N_3 K_3}{\omega_{\mathrm{F},2} \omega_{\mathrm{S},3}} \cdot \frac{(N_2 K_2 - \omega_{\mathrm{F},2})(N_2 K_2 - \omega_{\mathrm{S},3})}{(N_2 K_2 - N_3 K_3)} \tag{A.15}$$

This equation is a second-degree polynomial equation in function of $\omega_{S,3}$, which two solutions sum and product can be expressed by Eqs. (A.16) and (A.17):

$$\text{sum} = N_2K_2 + m_{II} \cdot \frac{N_3K_3}{\omega_{F,2}} - K_2 rm_{F,LSC} C_{F,2} \cdot \frac{N_3K_3 - N_2K_2}{\omega_{F,2} - N_2K_2} \quad \text{(A.16)}$$

$$\text{prod} = m_{II} \cdot \frac{N_2K_3N_3K_3}{\omega_{F,2}} \quad \text{(A.17)}$$

The solution verifying Eq. (5) will be chosen. All the parameters of the upper right part of the triangle have been determined.

$r < r_C$

This last part of the triangle corresponds to the stabilization of shock wave 2 in zone III and to the stabilization of a concentration composition part of dispersive wave 2 generated in zone II. The concentration composition of the dispersive wave is characterized by a couple of variables: ω_2, ω_3. The mass balance Eqs. (14) and (15) written on compounds 2 and 3 lead to Eqs. (A.18) and (A.19):

$$rm_{F,LSC} C_{F,2} = \frac{(N_2K_2 - \omega_2)^2(N_2K_2 - \omega_3)}{N_2K_2^2(N_2K_2 - N_3K_3)} \quad \text{(A.18)}$$

$$rm_{F,LSC} C_{F,3} = \frac{(N_3K_3 - \omega_2)^2(N_3K_3 - \omega_3)}{N_3K_3^2(N_3K_3 - N_2K_2)} \quad \text{(A.19)}$$

By rearranging Eqs. (A.18) and (A.19), it is possible to get Eqs. (A.20) and (A.21):

$$1 = \frac{rm_{F,LSC} C_{F,2}/N_2}{\left(1 - \frac{\omega_2}{N_2K_2}\right)^2} + \frac{rm_{F,LSC} C_{F,3}/N_3}{\left(1 - \frac{\omega_2}{N_3K_3}\right)^2} \quad \text{(A.20)}$$

$$\omega_3 = N_3K_3 - \frac{rm_{F,LSC} C_{F,3}}{N_3} \cdot \frac{(N_3K_3 - N_2K_2)}{\left(1 - \frac{\omega_2}{N_3K_3}\right)^2} \quad \text{(A.21)}$$

These last two equations can be solved numerically in order to calculate the corresponding unknown ω variables. These values are used to determine the value of m_{II}, which is characterized by Eq. (A.22):

$$m_{II} = \frac{(\omega_2)^2\omega_3}{N_2K_2N_3K_3} \quad \text{(A.22)}$$

The flow-rate ratio m_{II}, is given by Eq. (A.7). One may observe on Eqs. (A.20)–(A.22), that when the feed flow-rate ratio tends to zero, the variables ω_2 and ω_3, respectively, tend to N_2K_2 and N_3K_3. The flow-rate ratio m_{II} tends consequently to N_2K_2. Finally, in order to characterize entirely the four-zone TMB, the remaining unknown ω variables of zone III have to be determined, and this is related to the resolution of Eqs. (A.23) and (A.24) resulting from the mass balance Eqs. (14) and (15) written on compound 1:

$$m_F + m_{II} = m_{III} = \frac{\omega_{L,1}\omega_{L,2}}{N_1K_1} \quad \text{(A.23)}$$

$$rm_{F,LSC} \cdot C_{F,1} = \left(\frac{\omega_{L,2}}{N_1K_1} - 1\right) \cdot \left(1 - \frac{\omega_{L,1}}{N_1K_1}\right) \quad \text{(A.24)}$$

Eqs. (A.23) and (A.24) result in a second-degree polynomial equation, which solutions corresponds to the two involved variables. The expression of their sum and product is given by Eqs. (A.25) and (A.26):

$$\omega_{L,1} + \omega_{L,2} = K_1 rm_{F,LSC} C_{F,1} + N_1K_1 + m_{III} \quad \text{(A.25)}$$

$$\omega_{L,1}\omega_{L,2} = N_1K_1m_{III} \quad \text{(A.26)}$$

This completes the construction of the working triangle for the ternary four-zone TMB (case KEY = 1).

CASE KEY = 2

The complete determination of the triangle and the ω variables linked to each case can be performed thanks to the application of the mass balance equations on compounds 1–3 on the feed node (14) and interfaces I1 and I2 (15). The results depend on the different cases of stabilization of shocks 2 and 3 in zone III and dispersive waves 2 and 3 in zone II. In the following discussion, the determination of the triangular working region of a ternary four-zone TMB (Case KEY = 2) will be explained briefly because the methodology to be applied is the same as the one exposed for case KEY = 1.

Left part of the triangle

The expression (A.27) of m_{II} is given by the lower border value shown in Table 1.

$$m_{II} = \frac{N_2 K_2 \omega_{S,3}}{N_3 K_3} \quad (A.27)$$

The expression of variable $\omega_{S,3}$ is given by Eq. (A.28) obtained from the mass balance Eqs. (14) and (15) written on compound 3.

$$\omega_{S,3} = N_3 K_3 \cdot \left(1 - r m_{F,LSC} C_{F,3} \cdot \frac{K_3}{N_3 K_3 - N_2 K_2}\right) \quad (A.28)$$

By substituting (A.28) into (A.27), the expression of m_{II} in function of known variables is reached. The value of m_{III} is obtained from Eq. (A.7).

The last two remaining ω variables can be obtained by solving the mass balance Eqs. (A.29) and (A.30) obtained from Eqs. (14) and (15) written on compounds 1 and 2.

$$r m_{F,LSC} C_{F,1} \cdot K_1 (N_1 K_1 - N_2 K_2) = m_{III} N_2 K_2 \cdot \left(\frac{N_1 K_1}{\omega_{S,1}} - 1\right) \cdot \left(\frac{N_1 K_1}{\omega_{S,2}} - 1\right) - (N_1 K_1 - \omega_{S,1})(N_1 K_1 - \omega_{S,2}) \quad (A.29)$$

$$r m_{F,LSC} C_{F,2} \cdot K_2 (N_2 K_2 - N_1 K_1) = m_{III} N_1 K_1 \cdot \left(\frac{N_2 K_2}{\omega_{S,1}} - 1\right) \cdot \left(\frac{N_2 K_2}{\omega_{S,2}} - 1\right) - (N_2 K_2 - \omega_{S,1})(N_2 K_2 - \omega_{S,2}) \quad (A.30)$$

Right part of the triangle

The critical feed flow-rate expressed by Eq. (A.31) is obtained from Eqs. (14) and (15) written on compound 3 with, respectively, the lower and higher border value of m_{II} and m_{III}, taken from Table 1.

$$m_{F,C} = \frac{N_3}{C_{F,3}} \cdot \left(1 - \frac{\omega_{F,3}}{N_3 K_3}\right)^2 \quad (A.31)$$

$r > r_C$

The expression of m_{II} (A.32) is obtained from Eqs. (14) and (15) written for compound 3, considering that the omega rules lead to $\omega_{S,3} = \omega_{F,3}$.

$$m_{II} = \omega_{F,3} \cdot \left(1 - r m_{F,LSC} C_{F,3} \cdot \frac{K_3}{N_3 K_3 - \omega_{F,3}}\right) \quad (A.32)$$

The expression of m_{III} is given from Eq. (A.7). Eqs. (A.29) and (A.30) are solved to get the values of variables $\omega_{S,1}$ and $\omega_{S,2}$.

$r < r_C$

A composition of dispersive wave 3 is stabilized inside zone II. This is then characterized by a variable ω_3 and the expression of m_{II} is given by Eq. (A.33).

$$m_{II} = \frac{\omega_3^2}{N_3 K_3} \quad (A.33)$$

Eq. (A.34) gives the value of ω_3 and is obtained by using Eq. (A.33) into Eqs. (14) and (15) written on compound 3.

$$\omega_3 = N_3 K_3 \cdot \left(1 - \sqrt{\frac{r m_{F,LSC} C_{F,3}}{N_3}}\right) \quad (A.34)$$

Eq. (A.35) is reached by replacing Eq. (A.34) into Eq. (A.33).

$$m_{II} = N_3 K_3 \cdot \left(1 - \sqrt{\frac{r m_{F,LSC} C_{F,3}}{N_3}}\right)^2 \quad (A.35)$$

The expression of m_{III} is obtained from Eq. (A.7). The value of the remaining unknown $\omega_{S,1}$ and $\omega_{S,2}$ variables are obtained by resolving Eqs. (A.29) and (A.30). In conclusion, the complete determination of the triangular working region of a ternary four-zone TMB has been given.

References

[1] D.B. Broughton, US Pat. 2 985 589 (1961).
[2] A. Nicolaos, L. Muhr, P. Gotteland, R.-M. Nicoud, M. Bailly, J. Chromatogr. A 908 (2000) 71.
[3] A. Navarro, H. Caruel, L. Rigal, P. Phemius, J. Chromatogr. A. 770 (1997) 39.
[4] A.S.T. Chiang, AIChE. J. 44 (1998) 1930.
[5] Z. Ma, N.-H.L. Wang, R. Wooley, Ind. Eng. Chem. Res. 37 (1998) 3699.
[6] H.-K. Rhee, in: D. Tondeur, A.E. Rodrigues (Eds.), Equilibrium theory of Multicomponent Chromatography in Percolation Process: Theory and Application, 1985, Sijthoff & Noordhoff, Rockville, p. 285.
[7] H.-K. Rhee, R. Aris, N.R. Amundson, Phil. Trans. R. Soc. London A 269 (1971) 187.

[8] G. Storti, M. Mazzotti, M. Morbidelli, S. Carra, AIChIE J. 39 (1993) 471.
[9] M. Mazzotti, G. Storti, M. Morbidelli, AIChE J. 40 (1994) 1825.
[10] A. Gentilini, C. Migliorini, M. Mazzotti, M. Morbidelli, J. Chromatogr. A 805 (1998) 37.
[11] M. Mazzotti, G. Storti, M. Morbidelli, AIChE J. 42 (1996) 2784.
[12] M. Mazzotti, G. Storti, M. Morbidelli, J. Chromatogr. A 786 (1997) 309.
[13] M. Mazzotti, G. Storti, M. Morbidelli, J. Chromatogr. A 769 (1997) 3.
[14] M. Mazzotti, G. Storti, M. Morbidelli, AIChE J. 43 (1997) 64.